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Analysis of the pressure dependence of some thermodynamic properties of NaCl-structure alkali halide crystals using Woodcock potential

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Abstract The applicability of the Woodcock potential form is considered for studying the effect of the pressure of NaCl crystal. This potential form represents the composite form of the inverse power dependence and exponential dependence of the repulsive energy on interionic distance. Pressure dependence of Debye temperature, volume expansion coefficient and pressure – volume relation are calculated for NaCl crystal. The results are discussed and compared with available experimental data.

Keywords Alkali halide crystals, Woodcock potential, thermodynamic properties

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1 Introduction

The quantum mechanical calculation for the repulsive interaction energy between a pair of multi-electron atoms or ions is an extremely difficult and complicated task even for the simple condensed systems of closed shell ions such as NaCl-like alkali halides. Semiempirical and phenomenological potential forms have therefore been developed which represent the exponential dependence on interionic distance such as the Born Mayer exponential form, and the inverse power dependence as the Born-Lande inverse power form. Studies on the alkali halides provide a critical test of different interionic potentials. Woodcock [1] proposed a composite form for the repulsive interaction energy and demonstrated its applicability in alkali halide molecules and crystals by calculating the binding energy and compressibility. The Woodcock potential has been subsequently applied by Michielsen *et al.* [2] to study the molecular dynamics of molten salts. In the present paper, we investigate the applicability of Woodcock potential by calculating some physical quantities under the effect of pressure. Theory and method of calculation are given in Section 2.

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2. Theory and method of calculation

The lattice energy for an ionic crystal in terms of an effective pair potential is written as follows [2]

$$\varphi(r) = -\frac{\alpha_M e^2}{r} + \frac{B}{r^n}\exp\left(-\frac{r^m}{\rho}\right) - \frac{C}{r^6} - \frac{D}{r^8}, \qquad (1)$$

where r is interionic distance. The first term on the right hand side of (1) is the long-range electrostatic Madelung energy term, second represent the short-range overlap repulsive interaction, and the last two terms represent the Van der Waals dipole-dipole and dipole-quadrupole interactions. Following Michielsen *et al* [2], we take $n = 4$ and $m = 1$ so that

$$\varphi(r) = -\frac{\alpha_M e^2}{r} + \frac{B}{r^4}\exp\left(-\frac{r}{\rho}\right) - \frac{C}{r^6} - \frac{D}{r^8}. \qquad (2)$$

This choice of pair potential is simple and preferable over others mainly because such simple exponentials as in the overlap repulsive potential (2) also arise, *e.g.*, in the Heitler-London calculations for the hydrogen molecule. Moreover, the factor r^{-4} takes proper account of the polarization energy term [1]. The repulsive parameters B and ρ are calculated from ultrasonic

data [3] and the usual method based on the equation of state [4] Values of adjustable parameters for the different salts are given in Table 1.

Table 1a-b. Calculated values of Woodcock potential parameters and input data

1a

Crystal	Input experimental data [10]			Calculated Values of repulsive parameters	
	r_0	C	D	B	ρ
		10^{-60}	10^{-76}	10^{-8}	10^{-8}
	Å	erg/mole	erg/mole	erg cm^4	cm
LiF	2 014	18	11	0 839	552
LiCl	2 570	113	104	6 226	588
LiBr	2 751	183	190	11 36	577
LiI	3 000	363	470	24 36	564
NAF	2 317	46	31	3 909	558
NaCl	2 820	180	180	17 60	550
NaBr	2 989	271	300	24 58	573
NaI	3 237	482	630	54 02	552
KF	2 674	167	150	15 42	525
KCl	3 147	452	560	48 89	540
KBr	3 298	605	800	53 59	583
KI	3 533	924	1420	83 50	599
RbF	2 815	228	290	26 95	524
RbCl	3 291	691	960	83 70	543
RbBr	3 445	898	1340	108 4	530
RbI	3 671	1330	2240	134 6	587

1b

Input data for NaCl crystal [2]

	B_1	δ_1	β_0
NaCl	(10^{10}Pa)	10^{-1}	10^{-4} K^{-1}
	240	4 25	1 169

2.1 On the pressure dependence of Debye temperature :

Knowledge of the pressure dependence of the Debye temperature is needed in calculating the recoilless fraction of γ-ray emission or absorption in the Mossbauer effect [5]. There are no experimental data on the pressure dependence of the Debye temperature.

Based on a simple theory, Kumar and Dass [6] have obtained the following relation for the Debye temperature as a function of pressure :

$$\frac{\theta_P}{\theta_0} \quad 1+\left(\frac{\gamma_G}{B_T}\right. \tag{3}$$

where θ_p is the Debye temperature at pressure P. γ . B_1 and θ_0 refers to the Grüneisen constant, isothermal bulk modulus and Debye temperature, respectively, at zero pressure. Kumar and Dass made simple calculations of $\left(\frac{\theta_p}{\theta_0}\right)$ for sodium chloride from eq (3) These results could not be compared with experimental data since, as mentioned above, experimental data are not available. We have calculated θ_p by means of the γ_G Grüneisen parameter which is obtained from Woodcock potential [4] and we took experimental values of B_T and θ_0 as the input parameters. The change of θ_p with respect to P for alkali halides which we are interested in, are given in Table 2a The corresponding θ_p / θ_0 (Unit less) ratios of Lithium, Sodium and Rubidium halide crystals at $P = 3$ kbar and $T = 300$ K are also given in Table 2b for the sake of comparison The change of θ_p with respect to P for Rb, Li, K halides are almost linear. Among Na halides, only NaCl shows a little bit disagreement.

Table 2a. On the pressure dependence of Debye temperature of alkali halides at P(Kbar) $T = 300$ K

P	θ_P / θ_0 NaCl	P	θ_P / θ_0 NaI	P	θ_P / θ_0 NAF
0	1	0	1	0	1
1	1 00876	1	1 01503	1	1 00429
2	1 01759	2	1 03006	2	1 00858
3	1 02639	3	1 04509	3	1 01287
4	1 03624	4	1 06013	4	1 01716
5	1 04399	5	1 07516	5	1 02145
P	**θ_P / θ_0 LiF**	**P**	**θ_P / θ_0 LiCl**	**P**	**θ_P / θ_0 LiBr**
0	1	0	1	0	1
1	1 00276	1	1 00735	1	1 00947
2	1 00552	2	1 01470	2	1 01894
3	1 00828	3	1 02206	3	1 02842
4	1 01104	4	1 02941	4	1 03789
5	1 01380	5	1 03676	5	1 04737
P	**θ_P / θ_0 RbCl**	**P**	**θ_P / θ_0 RbBr**	**P**	**θ_P / θ_0 RbI**
0	1	0	1	0	1
1	1 01500	1	1 01798	1	1 02144
2	1 03000	2	1 03597	2	1 04288
3	1 04050	3	1 05396	3	1 06432
4	1 06002	4	1 07195	4	1 08576
5	1 07502	5	1 08993	5	1 10720

Table 2b. Comparison between calculated and experimental θ_P / θ_0 (Unit less) ratios of lithium, sodium and rubidium halide crystals at $P = 3$ Kbar $T = 300$ K

Crystal	θ_P / θ_0 (Unit less)		
	This work	Theory [11]	Experiment [11]
LiF	1 00828	1 0074	1 0085
LiCl	1.02206	1 0183	1 0225
LiBr	1 02842	1 0248	1 0292
NaF	1 01287	1 0099	1 0074
NaCl	1 02639	1 0198	1 0145
NaI	1 04509	1 0340	1 0282
RbCl	1 04050	1 0267	0 9994
RbBr	1.05396	1 0328	0 9984
RbI	1 06432	1 0446	0 9960

2.2 On the pressure dependence of volume thermal expansion coefficients :

The volume thermal expansion coefficient can be expressed as follows [7] :

$$\frac{\beta}{\beta_0} = \left(\frac{V}{V_0}\right)^{-\delta_T} \tag{4}$$

where β_0, δ_T refers to the volume thermal expansion coefficient at zero pressure and isothermal Anderson Gruneisen Delta β_0, δ_T are the input parameters [2] and V/V_0 ratio is calculated from the derivative of Woodcock potential [8] Values of $\left(\frac{\beta}{\beta_0}\right)$ are calculated and compared with experimental data in Table 3

where B_0, B_0' refers to isothermal bulk modulus and its first derivative B_0 is the input parameter at zero pressure B_0' is calculated from the Woodcock potential [9]. Values of $\left(\frac{V}{V_0}\right)$ are calculated and compared with experimental data in Table 3

3. Results and discussion

We have thus performed calculations for the pressure dependence of Debye temperature and pressure dependence of various crystalline properties of sixteen NaCl-structure alkali halides using Woodcock potential form

In Table 2a, The pressure variation of Debye temperature is a small effect Typically, a change of about 1 to 3% is observed in the Debye temperature for a pressure change about 3 Kbar

Table 3. On the pressure dependence of volume thermal expansion coefficient β, the isothermal bulk modulus B_T and pressure-volume relation V/V_0 of NaCl-crystal at $P(10^8$ Pa), T = 300 K

P 10^8pa	V/V_0 This Work	V/V_0 Theory [13]	V/V_0 Exp [12]	β $10^{-4}K^{-1}$ This Work	β $10^{-4}K^{-1}$ Theory [14]	β $10^{-4}K^{-1}$ Exp [12]	B_T (10Pa) This Work	B_T (10Pa) Theory [15]	B_T (10Pa) Exp [12]
0	1	1	1	1.169	1.169	1.169	238.41	238.41	238.41
10	0.9628	0.962	0.963	0.958	0.932	0.98	297.60	291	298.5
20	0.9331	0.932	0.932	0.819	0.770	0.83	357.47	340	357.0
30	0.9083	0.906	0.907	0.713	0.651	0.73	418.48	386	415.0
40	0.8873	-	0.883	0.632			479.85	431	
50	0.8690			0.398			542.07	475	
100	0.8029		0.788	0.288		-	861.10	677	-
150	0.7597		-	0.224			1196.0		
200	0.7281		0.701	0.183			1525.8	-	
250	0.7033			0.163			1868.7		
283	0.6895		0.650						

2.3 On the pressure dependence of isothermal bulk modulus

The isothermal bulk modulus can be expressed as follows [7]

$$\frac{B_T}{B_0} = \left(\frac{V}{V_0}\right)^{\delta_T} \tag{5}$$

where B_0 is the value of B_T at the starting point. B_0, δ_T are the input parameters [2] and V/V_0 ratio is calculated from the derivative of Woodcock potential [8]. Values of $\left(\frac{B_T}{B_0}\right)$ are calculated and compared with experimental data in Table 3

2.4 Pressure- volume relation :

Value of (V/V_0) is calculated using the following relation [7] :

$$= \exp\left(-\frac{1}{B_0'}\ln\left(1+\frac{B_0'}{B_0}P\right)\right. \tag{6}$$

The pressure variation of Debye temperature is ion-size dependent. The pressure variation increases as the size of the halogen ion increases On the other hand, for a given halogen ion, the pressure variation of the temperature decreases as the size of the caution increases θ_P/θ_0 (Unit less) ratios of Lithium, Sodium and Rubidium halide crystals calculated from (1) at P = 3 kbar and T = 300 K and they are given in Table 2b. From Figure 1, it can be seen that lithium and sodium halides are in good agreement with the experimental data but rubidium halides shows a little bit disagreement

The values of V/V_0, β and B_T are calculated under the effect of pressure from 0 to 250 (10^8 Pa) for the NaCl-crystal. Calculated values of V/V_0 are obtained with the similar results from the theory [13]. Both of them agree with experimental data. Volume thermal expansion coefficient and isothermal bulk modulus are better than those from the Theory [14, 15]. We note from Table 3 that the agreement between calculated and experimental values for various quantities is sufficiently good. We may thus conclude

that the Woodcock pair potential model, which has already been used successfully in predicting the properties of molecules [1] and molecular dynamics of molten salts [2], is also capable of yielding good agreement for thermodynamic approximations. Thus, it is found that the thermodynamic approximations discussed in the present work, can be used for studying high-pressure physics of solids.

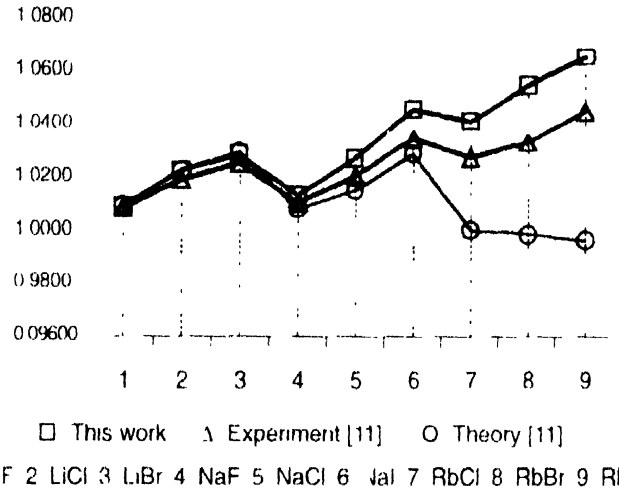

Figure 1. Comparison between calculated and experimental θ_p / θ_0 (Unit less) ratios of lithium, sodium and rubidium halide crystals at P = 3 kbar and T = 300 K.

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